about 1.90[25] to about 2.30.[26] The former value has been determined from thermochemical data by the method of Pauling[27] and has been shown[26] to be artificially low if silicon forms p → d π bonds with oxygen, fluorine, etc., as is almost certain. The upper limit comes from Mulliken–Jaffé values for the sp^3 (te) valence state. Since d orbitals lie at higher energies than s and p orbitals, their inclusion in the hybridization will result in lower electronegativity values.[28] The only direct evidence for a silicon electronegativity higher than that of hydrogen is the work of Quane[26] based on a Pauling-type calculation from bond energies of silanes in which π bonding is impossible. Unfortunately, uncertainties in bond energies and the limited number of compounds available place rather wide error limits on his estimates.

We have performed calculations[29] using electronegativity values of both 1.90 Pauling (= 6.26 V, Mulliken) and 2.25 Pauling (= 7.30 V, Mulliken). Our results range from 0.2, Si–C+→ (χ = 2.25), to 2.2 D, C–Si+→ (χ = 1.90). The interesting result of the calculations is to indicate that *the lower the electronegativity of silicon the greater is the total* CH_3SiH_3 *moment*, in complete contradiction to the prediction based on the Si–C+→ moment alone, but in agreement with the empirical bond moment work which gives the Si–H+→ moment the dominant effect in the total molecular moment. The empirically determined bond moments have "built-in" accommodations for the greater polarizability of silicon, the longer Si–H bond length, the electroneutrality principle, and similar factors treated implicitly by the Mulliken–Jaffé electronegativity treatment.

Finally, we would call attention to the statement of Liskow and Schaefer[6] that although the expectation value of the dipole moment operator clearly indicates the molecular moment is in the direction CH_3SiH_3+→, point charges obtained from their Mulliken populational analysis yield a moment SiH_3CH_3+→. This is yet another example indicating that populational analysis fails to yield values corresponding to the chemist's concept of partial charge and should either be used cautiously or replaced by alternate methods.[22,23]

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[25] A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

[26] D. Quane, *ibid.*, **33**, 2722 (1971).

[27] Reference 7, Chapter 3.

[28] For example, see J. E. Huheey and J. C. Watts, *Inorg. Chem.*, **10**, 1553 (1971).

[29] We calculated the molecular moment using a point-charge approximation. We should like to thank a referee for reminding us to note that this approximation is valid only, as is the case with CH_3SiH_3, where lone pair moments can be ignored.[30]

[30] See F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972, pp 120–122; J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N. Y., 1972, pp 168–170.

Ab Initio Self-Consistent Field and Configuration Interaction Study of Beryllium Borohydride

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Abstract: Optimized geometries and relative energies are reported for many possible structures of beryllium borohydride. These calculations are at the *ab initio* minimum basis set self-consistent field level of approximation, with near optimum exponents. Configuration interaction calculations on the bound conformers with all valence shell single and double excitations included suggest that two or three conformers may coexist in the gas phase. This result is also based on the available experimental evidence. The previous experimental work on the gas phase is discussed in view of the above possibility.

The structure of gas-phase beryllium borohydride is currently one of the most interesting and frustrating problems in structural inorganic chemistry. To date at least six unique structures have been proposed, all of which have had some kind of experimental "verification." Although beryllium borohydride has been the subject of a few theoretical studies,[1,2] no extensive geometry optimizations using accurate molecular orbital techniques have yet been reported. In this paper we present a series of *ab initio* self-consistent field (SCF) and configuration interaction (CI) calculations on many possible conformers of this molecule and we report relative energies and optimized geometries for these conformers. By comparing our theoretical results with the available experimental data, we arrive at some tentative conclusions concerning the structure of this molecule in the gas phase.

Beryllium borohydride was first synthesized[3] by Burg and Schlesinger *via* the reactions

$$Be(CH_3)_2 \xrightarrow{B_2H_6} CH_3BeBH_4 \xrightarrow{B_2H_6} Be(BH_4)_2$$

They reported a vapor pressure of about 6 mm at room temperature and vapor density measurements which suggested that the gas phase is monomeric. Later, the monomeric nature of the gas phase was confirmed.[4] Remarkably, they also suggested that the crystalline phase might be polymeric. Our single-crystal X-ray

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[1] D. R. Armstrong and P. G. Perkins, *Chem. Commun.*, 352 (1968).

[2] G. Gunderson and A. Haaland, *Acta Chem. Scand.*, **22**, 867 (1968).

[3] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **62**, 3425 (1940).

[4] J. W. Nibler, *ibid.*, **94**, 3349 (1972).

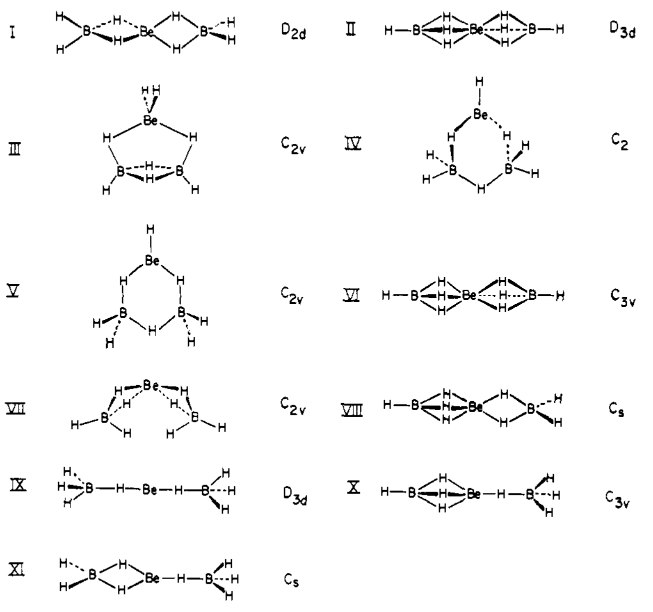

Figure 1. Possible structures of gas-phase beryllium borohydride.

diffraction study[5] later showed that the crystalline phase does indeed consist of polymers.

The first structural proposal for beryllium borohydride was made by Longuet-Higgins and Bell,[6] who suggested a structure with double hydrogen bridges and D_{2d} symmetry (structure I, Figure 1). An electron diffraction study[7] by Silbiger and Bauer was interpreted as giving evidence for a triple hydrogen bridge structure with D_{3d} symmetry (structure II, Figure 1), but a few years later the electron diffraction data were shown[8] to be consistent with I if the bridge hydrogens were unsymmetrical. An X-ray diffraction study[9] failed to yield a structure, but the correct space group and unit cell dimensions were reported. Perhaps because I strongly resembled the known diborane structure it became generally accepted and was not questioned for over 15 years.

In 1967 the electron diffraction work was repeated[10] and found to be consistent with a structure of C_{2v} symmetry (structure III, Figure 1). The radial distribution curve from this study was considerably different from the earlier curve and gave no evidence at all for a long boron–boron distance. Because of some highly unusual bond lengths (Be-H$_t$ = 1.61 and Be-H$_b$ = 1.99 Å), this structure was questioned and a new triangular structure (structure IV, Figure 1) was proposed[11] by Cook and Morgan. This proposal was made on the basis of infrared and mass spectrometry studies, and the structure was found to be consistent with the 1967 radial distribution curve. A specific conformer of IV was also proposed[12] (structure V, Figure 1). The dipole moment was determined independently by two dielectric measurements[13,14] and confirmed by an electric deflection experiment.[14] Both determinations gave large dipole moments ($\mu \sim 2.1$ D) and *apparently* eliminated the symmetrical structures I and II, which of course have a zero dipole moment. All dipole moment measurements were conducted at only one temperature. Subsequently, the electron diffraction work was again repeated by two groups and yet another radial distribution curve was obtained which did not agree with *either* the 1946 or 1967 curves. Instead, the data were found[15] to be consistent with either II (with different bond lengths than those of the 1946 proposal) or a new structure with C_{3v} symmetry (structure VI, Figure 1). This structure may be derived from II by displacing the beryllium toward one of the borons. About the same time a detailed infrared study[16] of the gas by Cook and Morgan was interpreted in terms of another structure (structure VII, Figure 1), in which two hydrogens were extremely close (about 0.6 Å). Finally, an infrared and Raman study[4] of the gas and matrix isolated compound by Nibler led to the important conclusion that at least two distinct conformers exist in the gas phase. One of these conformers was believed to be VI, while the other one could not be completely assigned but was consistent with I. Most significantly, the low frequency infrared spectrum was reported for the first time and was shown to consist of four bands in the 280–390-cm^{-1} region. Three of these bands were assigned to fundamentals on the basis of VI, including the strong band at 280 cm^{-1}. This band was assigned with confidence to the B–Be–B bending mode. Two attempts to record the microwave spectrum have yielded no spectrum at all.[17]

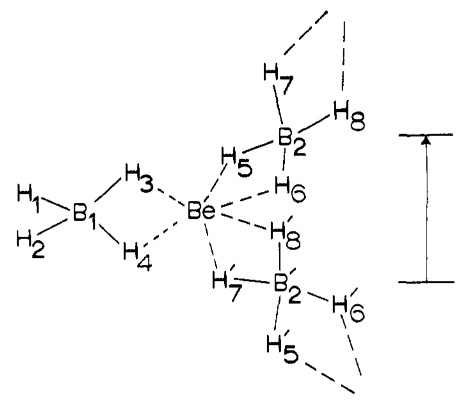

Figure 2. Chemical repeat of crystalline beryllium borohydride.

Meanwhile, Nibler, Shriver, and Cook reported[18] an infrared study of solid beryllium borohydride and proposed that the solid consisted of BH_4^- and BH_4Be^+ ions, with a double hydrogen bridge between boron and beryllium in BH_4Be^+. Our X-ray diffraction study[5] yielded a precise structure for the solid state. The solid consists of one dimensional helical polymers of alternating BH_4^- and BH_4Be^+ groups (Figure 2). There are double hydrogen bridges associated with *every* next neighbor boron–beryllium interaction. The hydrogen

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(5) D. S. Marynick and W. N. Lipscomb, *Inorg. Chem.*, **11**, 820 (1972); D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **93**, 2322 (1971).

(6) H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 250 (1943).

(7) G. Silbiger and S. H. Bauer, *J. Amer. Chem. Soc.*, **68**, 312 (1946).

(8) S. H. Bauer, *ibid.*, **72**, 622 (1950).

(9) A. J. Stosick, *Acta Crystallogr.*, **5**, 151 (1952).

(10) A. Almenningen, G. Gundersen, and A. Haaland, *Chem. Commun.*, 557 (1967).

(11) T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, **91**, 774 (1969).

(12) See T. H. Cook and G. L. Morgan, *ibid.*, **92**, 6493 (1970), footnote 11.

(13) J. W. Nibler and J. McNabb, *Chem. Commun.*, 134 (1969).

(14) J. W. Nibler and T. Dyke, *J. Amer. Chem. Soc.*, **92**, 2920 (1970).

(15) See ref 4, footnote 11.

(16) T. H. Cook and G. L. Morgan, *J. Amer. Chem., Soc.*, **91**, 774 (1967).

(17) See ref 4, footnote 9.

(18) J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.*, **54**, 5257 (1971).

coordination around beryllium was unambiguously determined to be a distorted trigonal prism, but the degree of ionic character in the solid is still open to question. Although the existence of double hydrogen bridges in the solid is highly suggestive of a gas-phase structure such as I, the solid-state structure clearly gives no *direct* information concerning the structure in the gas phase.

The impetus for the present work stems from the fact that although a great deal of structural work has been done, none of the above gas-phase structures can be considered to be established. If Nibler's multistructure hypothesis is correct, the electron diffraction results clearly cannot be taken too seriously. Even if there is only one gas-phase conformer, the probable existence of three or four fundamentals in the low frequency infrared implies that approximately 50% of the molecules are in excited vibrational states at room temperature. Again, this fact would seriously complicate the interpretation of the electron diffraction results. The exact dipole moment is also in question, since the gas phase may be a mixture of vibrational states. Nibler's infrared and Raman results are complicated by the possible existence of *three* unique conformers (see below) and decomposition products such as $BeBH_5$ and $H_2BH_2BeH_2BeH_2BH_2$, in addition to the known diborane contamination. The problems in interpreting other infrared results are discussed in detail by Nibler.[4]

Calculations

The SCF calculations were performed with Stevens' program[19] on an IBM 360/195 computer. A minimum basis set of Slater orbitals was employed. For structures I and II, the structural parameters and orbital exponents were chain optimized. Estimated errors are ±0.02 Å for bond lengths, ±3° for bond angles and ±0.01 for orbital exponents. The minimum basis set energies for I and II are estimated to be within 0.5 kcal/mol of the optimum values. The optimized exponents of boron, beryllium, and bridge hydrogens for I and II (Table I) were averaged to obtain a set of standard exponents (Table II). These exponents were used in all calculations on the other conformers and were not optimized for each structure. Recalculation of the energies of I and II using the standard exponents yielded a maximum error of 0.25 kcal/mol and an error in the energy difference of only 0.06 kcal/mol. The standard exponent for terminal hydrogens bound to beryllium was taken as the optimized value for IV. For bridge hydrogens between two borons, the optimized diborane exponent[20] was used. The orbital exponent for the single Be–H–B bridging hydrogen in structures IX, X, and XI was taken as the optimized value for IX at the initial geometry (see below). All geometrical parameters of most conformers were chain optimized until the energy changed less than 0.5 kcal/mol and the bond lengths less than 0.02 Å after a complete cycle of optimization, unless the molecule dissociated. Each calculation took full advantage of molecular symmetry. As geometrical parameters were varied, only the integrals that changed were recalculated.

Table I. Optimized Exponents for Structures I and II

	I	II
H_t	1.134	1.148
H_b	1.145	1.132
B_{1s}	4.688	4.688
B_{2s}	1.436	1.452
B_{2p}	1.454	1.453
Be_{1s}	3.700	3.705
Be_{2s}	1.240	1.249
Be_{2p}	1.260	1.232

Table II. Standard Exponents

Atom[a]	Exponent	Source
Be-H_t	1.05	Optimized for IV
B-H_t	1.13	Optimized for I
Be-H-B	1.10	Optimized for IX
BH_2Be	1.14	Av of I and II
BH_3Be		
B-H-B	1.209	Optimized for diborane
B_{1s}	4.688	Av of I and II
B_{2s}	1.44	
B_{2p}	1.45	
Be_{1s}	3.70	
Be_{2s}	1.24	
Be_{2p}	1.24	

[a] Exponents are for the atom in italics.

Table III. Optimized Coordinates[a]

	x	y	z
		I[b]	
H_t	1.9633	0.0	4.7222
H_b	0.0	1.9326	2.0391
B	0.0	0.0	3.6249
Be	0.0	0.0	0.0
		II[c]	
H_t	0.0	0.0	5.5213
H_b	−2.1653	0.0	2.3226
B	0.0	0.0	3.2951
Be	0.0	0.0	0.0
		IV[d]	
H_t	2.0531	−2.3503	2.7396
H_t'	0.5329	3.7975	0.3130
H_{tBe}	0.0	0.0	7.3989
H_b	0.0	0.0	0.3597
H_b'	1.7157	1.9700	3.3814
B	0.0	2.1399	1.7520
Be	0.0	0.0	4.9776
		V[a]	
H_t	0.0028	3.1894	1.9777
H_b	−0.2125	0.0	0.0
H_b'	3.1080	3.0000	0.0
B	0.6614	2.3259	0.0
Be	4.5951	0.0	0.0
		VIII	
H_t	0.0	0.0	−5.5185
H_b	2.1770	0.0	−2.1955
H_b	−1.0802	1.8748	−2.3533
H_b	−1.0802	−1.8748	−2.3533
H_t	1.9637	0.0	4.7328
H_t	−1.9646	0.0	4.7303
H_b	0.0	1.9287	2.1036
H_b	0.0	−1.9287	2.1036
B	0.0	0.0	3.6334
B	0.0	0.0	−3.2950
Be	0.0	0.0	0.0

[a] Atomic units. [b] The symmetry planes are xy, xz, and yz. [c] The C_3 axis is along z. [d] The C_2 axis is along z. [e] The C_2 axis is along x.

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(19) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(20) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *ibid.*, **51**, 2085 (1969).

Table IV. Population Analysis[a]

Structure	Atom[b]	Charge
I	$\mathrm{H_t}$	−0.07
	$\mathrm{H_b}$	−0.11
	B	0.05
	Be	0.61
II	$\mathrm{H_t}$	−0.04
	$\mathrm{H_b}$	−0.08
	B	−0.08
	Be	+0.70
IV	B-H_t	−0.08
	B-H_t'	−0.04
	Be-H_t	−0.28
	B-H_b-B	−0.03
	B-H_b-Be	−0.09
	B	0.03
	Be	0.67
V	B-H_t	−0.07
	Be-H_t	−0.28
	B-H_b-B	−0.08
	B-H_b-Be	−0.18
	B	0.15
	Be	0.68
VIII	B-H_t	−0.04
	H_t / B \ $\mathrm{H_t}$	−0.07
	$\mathrm{H_t}$ / B \ H_t	−0.07
	H / \ B Be \ / $\mathrm{H_2}$	−0.08
	H / \ B Be \ / H_2	−0.07
	B-H_2-Be	−0.11 per H
	B	0.02
	Be	0.67

Structure	Bond	Overlap pop	Bond length[c]
I	B-$\mathrm{H_t}$	0.83	1.19
	B-$\mathrm{H_b}$	0.46	1.32
	Be-$\mathrm{H_b}$	0.34	1.49
	B-Be	0.25	1.92
II	B-$\mathrm{H_t}$	0.83	1.18
	B-$\mathrm{H_b}$	0.61	1.26
	Be-$\mathrm{H_b}$	0.18	1.68
	B-Be	0.35	1.74
IV	B-$\mathrm{H_t}$	0.76	1.21
	B-$\mathrm{H_t}'$	0.81	1.20
	Be-$\mathrm{H_t}$	0.78	1.28
	B-HB	0.43	1.35
	B-HBe	0.60	1.26
	BH-Be	0.22	1.62
	B-Be	0.17	2.05
	B-B	0.96	2.26
V	B-$\mathrm{H_t}$	0.83	1.20
	Be-$\mathrm{H_t}$	0.78	1.28
	B-HB	0.49	1.32
	B-HBe	0.43	1.30
	BH-Be	0.33	1.45
	B-Be	0.09	2.42
	B-B	0.08	2.46
VIII	B-$\mathrm{H_t}$	0.83	1.18
	$\mathrm{H_t}$ / B $\mathrm{H_t}'$	0.83	1.19
	$\mathrm{H_t}$ B \ $\mathrm{H_t}'$	0.83	1.19
	H / B Be \ H	0.48	1.30
	H \ B Be / H	0.31	1.51
	H / B Be $\mathrm{H_2}$	0.56	1.29
	H \ B Be H	0.22	1.64
	H B Be[d] \ $\mathrm{H_2}$	0.62	1.25
	H B Be[d] / $\mathrm{H_2}$	0.16	1.70
	B-Be	0.35	1.75[e]
	B-Be	0.25	1.92

[a] Standard exponents. [b] Charges are for the atom in italics. [c] In Å. [d] The notation B-$\mathrm{H_2}$ refers to one BH bond of the symmetry equivalent BH bonds in this structure type. [e] This distance has three hydrogen bridges.

Computing times for a single calculation varied from 2.8 min for VIII to 0.99 min for II.

CI calculations were performed on the bound conformers using the SCF optimized geometry and the standard basis set. All single and double excitations were included, except for excitations from the inner-shell orbitals of boron and beryllium. Computing times on a 360/91 varied from 2.5 to 9 min.

Results

Structure I. The optimized coordinates are given in Table III. The computed boron–beryllium distance of 1.918 Å is exactly the distance found for one of the boron–beryllium interactions in the solid state.[5] A population analysis using standard exponents (Table IV) indicates strong bonding of the bridge hydrogens to both boron and beryllium. In contrast to results obtained for boron hydrides, the bridge hydrogens are more negative than the terminal hydrogens. Also, considerable ionic character is indicated by the 0.56 e difference between the boron and beryllium charges. The SCF and SCF–CI energies are given in Table V.

Table V. Energetics

Structure	E_{SCF}[a,b]	ΔE_{SCF}[c]	VT[d]	$E_{\mathrm{SCF-CI}}$[a]	$\Delta E_{\mathrm{SCF-CI}}$[c]
I	−68.5109	0	1.0018	−68.6548	0
VIII	−68.4972	+8.6	1.0011	−68.6444	+6.5
II	−68.4931	+11.2	1.0009	−68.6431	+7.3
IV	−68.4670	+27.6	1.0025	−68.6116	+27.1
V	−68.4681	+26.9	1.0002	−68.6053	+31.0

[a] Atomic units. [b] Standard exponents. [c] Relative to structure I, kcal/mol. [d] $-E/T$.

We note that this is the lowest energy conformer of any we have explored. Because the B–Be–B bending mode has been assigned[4] to an infrared band at unusually low frequency, it is of considerable interest to examine the energy changes upon bending this molecule. In Table VI we present the relative energies and dipole moments for this conformer and structure II with B–Be–B angles of 0, 10, 20, and 30°. All of these calculations were at the SCF level of approximation (not CI corrected) and all bond lengths were assumed to be the same as the linear molecules. From comparison of structures I and II it is apparent that the D_{2d} structure is considerably more flexible with respect to the bending motion than is the D_{3d} structure. However, we cannot attach any quantitative significance to these energy differences and dipole moments because of the lack of geometry optimization at each angle and inadequacies in the basic set. Clearly the greater flexibility of the D_{2d} structure is expected on the basis of simple steric arguments.

Table VI. ΔE's and Dipole Moments for Bonding in Structures I and II[a]

	I			II		
	E[b]	ΔE[c]	D	E	ΔE[c]	D
0°	−68.5109	0	0.0	−68.4931	0.0	0.0
10°	−68.5099	+0.63	0.55	−68.4914	+1.07	0.54
20°	−68.5068	+2.57	1.10	−68.4865	+4.14	1.09
30°	−68.5012	+6.09	1.64	−68.4774	+9.85	1.62

[a] The molecules were bent in a direction which minimized steric interactions between bridge hydrogens. [b] Atomic units. [c] Relative to structure I at 0°, kcal/mol.

Structure II. The optimized geometrical parameters (Tables III and IV) are considerably different from those for structure I. Both bond lengths and overlap populations (Table IV) indicate very unsymmetrical Be–H$_b$–B bonds, with relatively short B–Be bonds (1.74 Å). The difference between boron and beryllium charges is 0.78 e, indicating even greater ionic character for this structure than for I. This molecule is 7.3 kcal/mol less stable than I by the SCF–CI criterion.

Structure III. Initial boron–boron and boron–beryllium distances were chosen to agree with the 1967 electron diffraction work.[10] A Be–H$_t$ distance of 1.3 Å was assumed, and the Be–H$_b$–B bridge hydrogen positions were optimized. At this point the calculated SCF energy was 125 kcal/mol higher than I. Attempts to optimize the position of the BeH$_2$ unit relative to the remainder of the molecule resulted in dissociation to B$_2$H$_6$ and BeH$_2$. Thus, this conformer is not bound at the minimum basis set SCF level of approximation.

Structure IV. The initial geometrical parameters were those assumed by Cook and Morgan.[11] Subsequent optimization yielded boron–boron and boron–beryllium distances of 2.26 and 2.05 Å, respectively (Table IV). The dipole moment computed from the SCF wave function is 0.51 D. This computed dipole moment may be in error by as much as a factor of two or more. The SCF–CI energy is 27.1 kcal/mol higher than I.

Structure V. The starting B–H and Be–H bond lengths were assumed to be the same as IV. The SCF–CI energy is 31.0 kcal/mol higher than I, and the SCF dipole moment is 0.25 D. The boron–boron and boron–beryllium distances (Table IV) are longer than those of IV.

Structure VI. Nibler has proposed[4] that the D_{3d} structure (II) actually represents a local *maximum* on the BeB$_2$H$_8$ energy surface, and that a double minimum exists with unequal boron–beryllium distances and C_{3v} symmetry (structure VI). The displacement of beryllium toward one of the borons was estimated to be roughly 0.2 Å. We have searched for such a structure by the following procedure: (1) an initial guess of the two boron–beryllium distances was made, (2) the positions of the two sets of triple hydrogen bridges were fully optimized while keeping the boron–beryllium distance fixed, and (3) the positions of the two BH$_4$ groups were independently optimized with respect to the beryllium. Three sets of initial boron–beryllium distances were tried (1.95, 1.65; 2.0, 1.7; and 2.025, 1.625 Å). These distances appear reasonable since it is extremely unlikely that any gas-phase structure of this type could have a boron–beryllium distance of less than 1.6 or greater than 2.0 Å. In each case a careful geometry optimization resulted in the return of the molecule to the symmetric D_{3d} configuration (II). No unsymmetrical structure could be found which had a lower energy than II. The symmetric D_{3d} structure therefore appears to be a local *minimum* on the SCF energy surface.

Structure VII. Although this structure can surely be eliminated on the basis of steric arguments alone, a few trial calculations were attempted. All bond lengths were assumed to be equal to those of I. Using a B–Be–B angle of 60°, the calculated SCF energy was 761 kcal/mol higher than I. Optimization of the B–Be–B angle resulted in a linear molecule of D_{2h} symmetry with an SCF energy 14.7 kcal/mol higher than I. No further geometry optimizations were done, but we note that 14.7 kcal/mol is an upper bound for the minimum basis set SCF value of the rotation barrier in the D_{2d} molecule (I).

Structure VIII. This conformer, which may be considered to be a hybrid of I and II, has not been seriously considered previously. Initial geometrical parameters were taken from structures I and II. Assuming the molecule is linear, all other parameters were optimized once. The net gain in energy was only 0.6 kcal/mol. The B–Be–B angle was optimized by the

PRDDO method and found to be within 2° of linearity; therefore, no further *ab initio* optimizations were deemed necessary, and the molecule was constrained to be linear. We estimate that our calculated SCF energy is within 1 or 2 kcal/mol of the true minimum basis set energy. The SCF–CI energy is 6.5 kcal/mol higher than I. Calculation of the dipole moment from the SCF wave function yields 0.79 D.

Structure IX. A linear B–H_b–Be–H_b–B arrangement with tetrahedrally coordinated boron and D_{3d} symmetry was assumed initially. The B–H_b and Be–H_b distances were 1.3 and 1.5 Å, respectively. Chain optimization of the B–H_b and Be–H_b distances and the H_b–B–H_t angle resulted in dissociation to $2BH_3$ and BeH_2.

Structure X. The starting geometry was the same as IX for the single bridge side of the molecule and the same as II for the triple bridge side. Optimizations analogous to those for IX resulted in dissociation into $BeBH_5$ and BH_3, although a shallow minimum (less than 1.0 kcal) appears to exist for a $H_b \cdots BH_3$ distance of about 2–3 Å.

Structure XI. Geometrical parameters were obtained from I and IX, and once again optimization resulted in dissociation to $BeBH_5$ and BH_3.

Discussion.

Before we discuss the implications of these results, we must first consider two important questions: what experimental evidence can be considered reliable, and how accurate are the calculations presented here?

From examination of the experimental work we must conclude that none of the structures of Figure 1 can be considered to be fully established. For this reason we intentionally did not use experimental evidence to eliminate possible structures from our theoretical study. Instead we have optimized every conformer which has been previously proposed or which is chemically reasonable. We can, however, infer a few relevant facts from the experimental work. First, in every infrared study published the existence of bands which can be attributed to BH_2 groups and BeH_2B groups is evident. Thus it appears very likely that there exists at least one conformer with the above structural features. Second, it appears likely that there exists more than one gas-phase structure. This inference was made[4] on the basis of the absence or near absence of several bands when the gas is trapped at very low temperatures in a matrix of solid argon or nitrogen. Effects such as matrix orientation, hot bands, and structural changes upon condensation were almost certainly eliminated. Finally, the gas phase is probably largely monomeric.

The question concerning the accuracy of the calculations is even more difficult to answer. Very few calculations on polyatomic systems at the minimum basis set SCF–CI level of approximation have been done. We can, however, draw some conclusions from the BH_3–B_2H_6 system, which has been studied in some detail. The experimental ΔE for the reaction

$$2BH_3 \longrightarrow B_2H_6$$

is about −35 kcal/mol, but a minimum basis set SCF–CI calculation yields[21a] only −17 kcal/mol. Thus even at this relatively sophisticated level of approximation we still have an error of about 18 kcal/mol. This error, though large, is not surprising because (1) both borons are changing from three to four coordinate, and it is well known[22] that d orbitals (not included in the basis set) stabilize fourfold coordination preferentially, and (2) the change in the correlation energy for this reaction is known[21b] to be about −17 kcal/mol or about one-half the total ΔE. Clearly we cannot expect this limited CI to both make up for deficiencies in the basis set *and* account for the large correlation energy change. For beryllium borohydride the change in coordination involves only beryllium, which should be much less sensitive to the addition of d orbitals. Also, we have seen (Table V) that the CI corrections to the SCF energy *differences* are all rather small, and therefore it seems possible that the actual correlation corrections are small and that the basis set is adequate.

The implications of our theoretical results are as follows. Structures III, IX, X, and XI all dissociate upon optimization and therefore can be eliminated with certainty. Although the addition of CI may help to stabilize these molecules, their energies will still be considerably higher than I. Structure VII is clearly incorrect and need not be considered further. We find no evidence for the double minimum structure VI. Such a structure may be represented as $(HBH_3Be)^{\delta+}$-$(H_3BH)^{\delta-}$ and is clearly part way along the dissociative path to $BeBH_4^+$ and BH_4^-. This type of dissociation is handled correctly by a single determinate SCF wave function, and we would expect to see the double minimum if it exists. Of course if the barrier is sufficiently small ($\leqslant 3$ kcal/mol) it might not be reproduced by these calculations, but in this case we might expect to observe vibrational energy level splitting, which is not observed.[4] Structures IV and V are of comparable energy and are both calculated to be about 30 kcal/mol less stable than I. We therefore can eliminate these structures on the basis of energy alone, since we do not expect errors as large as 30 kcal. However, we also note that the optimized bond distances, which are expected to be given to within a few hundredths of an ångström by *ab initio* SCF calculations,[23] do not agree closely with the 1967 electron diffraction results on which IV was partly based. In fact, radial distribution curves calculated from the optimized parameters for IV and V *do not agree* at all with the 1967 curve. Therefore we find no solid theoretical or experimental evidence for these structures. Furthermore, the nearly vacant p orbital on beryllium in these conformers would probably result in the formation of stable dimers connected *via* double hydrogen bridges between the beryllium atoms.[24]

We are left with only three possible structures. One of them is our old friend[6,25] the D_{2d} structure (I). This structure is calculated to be the most stable, but it is followed closely by VIII ($\Delta E = +6.5$ kcal/mol) and II ($\Delta E = +7.3$ kcal/mol). These energy differences are too small to be meaningful, and we cannot pin down the most stable structure at this time. Indeed, the

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[21] (a) I. M. Pepperberg, D. A. Dixon, and W. N. Lipscomb, manuscript in preparation. (b) J. H. Hall, Jr., D. S. Marynick, and W. N. Lipscomb, *Inorg. Chem.*, **11**, 3126 (1972).

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experimental evidence strongly suggests that *at least* two of these structures may coexist in the gas. The large number of observed infrared and Raman bands can easily be explained if appreciable amounts of VIII exist. The observed dipole moment can also be accounted for by VIII. Although the electron diffraction experiments cannot give us the hydrogen positions, the recent work may well be correct to the extent that it requires *long* boron–boron distances, as found here. We also point out that the crystallization of I requires no hydrogen rearrangements. This is not true of any other structure considered, although the hydrogen rearrangements necessary in II and VIII are minimal.

Finally, it is well-known that many metal borohydrides undergo rapid intramolecular hydrogen tautomerism, making the hydrogens equivalent on the nmr time scale. Although the nmr spectrum of beryllium borohydride has not yet been observed, the three structures I, VIII, and II provide a convenient and obvious path for such a tautomerism.[26]

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[26] As this manuscript was being submitted a similar independent SCF–CI study on beryllium borohydride appeared: R. Ahlrichs, *Chem. Phys. Lett.*, **19**, 174 (1973). This study employs a Gaussian basis set and the independent electron pair approximation for correlation corrections. It does not consider structures III, VI, XI, X, or XI, no configuration interaction results are reported for structure IV or V, and structure IV was not optimized. Our basic conclusions are, however, very similar.

Mechanistic Studies of One- and Two-Equivalent Oxidations of the Mercury(I) Dimer

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Abstract: Kinetic studies on the reactions of mercury(I) dimer with the one-equivalent oxidants Fe(phen)$_3^{3+}$ and Ru(bipy)$_3^{3+}$ and the two-equivalent oxidant BrO$_3^-$ are described. These and other reactions of the mercury(I) dimer previously reported can be summarized as follows. One-equivalent oxidants usually react by a mechanism (Hg^{I})$_2$ + oxidant (1 e$^-$) → Hg^{I} + Hg^{II} and Hg^{I} + oxidant (1 e$^-$) → Hg^{II} (fast), with a rate law first order in (Hg^{I})$_2$ and oxidant. Two-equivalent oxidants react by a mechanism (Hg^{I})$_2$ $\rightleftharpoons$ Hg^0 + Hg^{II} (fast) and Hg^0 + oxidant (2 e$^-$) → Hg^{II}, with a rate law which is first order in both reactants, but which is in addition dependent on [Hg^{II}]$^{-1}$.

Different reaction sequences are generally observed in redox reactions involving one- and two-equivalent oxidants. As a result a distinction between the two based on differences in stoichiometry, reaction products, and/or rate law is often possible. Well-known examples are the reactions of one- and two-equivalent oxidants with hydrazine[1] and with sulfite,[2] where the stoichiometries and products often enable a clearcut distinction to be made.[3]

With mercury(I) dimer as reductant a similar distinction is not at present clearly defined.[4,5] Reactions of mercury(I) dimer with thallium(III),[6] cobalt(III),[7] manganese(III),[8] cerium(IV) (in the presence of sulfate[9] and catalyzed by silver(I)[10] and hexachloroiridate(III)[11]), and neptunium(VII)[5] have been studied previously. The mechanisms of the reactions of the one-equivalent oxidants tris(1,10-phenanthroline)iron(III) and tris(2,2′-bipyridine)ruthenium(III) and the two-equivalent oxidant bromate are considered in this paper. The stoichiometries (in equivalents) are the same and mercury(II) is the product in all cases. The rate laws differ, however, and with information from previous studies we feel it is now possible to differentiate between the two types of reactant.

Experimental Section

Preparation of Solutions of the Mercury(I) Dimer. Stock solutions of the perchlorate salt of (Hg^{I})$_2$ in perchloric acid (*ca.* 1 *M*) were prepared in three different ways. (i) Analar BDH mercury (23.5 g) and 50 ml of water were heated together in a 250-ml beaker, and concentrated nitric acid was added a little at a time to the hot solution until all the mercury dissolved. Nitrogen dioxide was given off. Mercury oxide, HgO, was precipitated by adding Analar anhydrous sodium carbonate. The HgO was dried by suction and then dissolved in 2 *M* HClO$_4$. The mercury(II) in solution was converted to mercury(I) dimer by shaking with a slight excess of mercury for *ca.* 24 hr.[12] (ii) Yellow HgO, May and Baker Labor-

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[1] See, for example, W. C. E. Higginson, *Chem. Soc., Spec. Publ.*, **No.** 10, 95 (1957).

[2] W. C. E. Higginson and J. Marshall, *J. Chem. Soc.*, 447 (1957).

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[5] M. A. Thompson, J. C. Sullivan, and E. Deutsch, *J. Amer. Chem. Soc.*, **93**, 5667 (1971). We note also that no reaction between mercury(I) dimer and neptunium(VI) is observed over *ca.* 1 hr at 50° with neptunium(VI) concentrations 100 times greater than reported in this paper (personal communication, J. C. Sullivan).

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